Letters to the Editor

The Board of Editors does not hold itself responsible for opinions expressed in the letters published in this section. The notes containing short reports of original investigations communicated to this section should not contain many figures and should not exceed 500 words in length. The contributions reaching the Secretary by the 15th of any month may be expected to appear in the issue for the next month. No proof will be sent to the author.

1

ON THE TRANSFER OF ELECTRONIC EXCITATION ENERGY IN LIQUIDS

M. K. MACHWE, J. KISHORE AND K. GOPALA KRISHNAN

Department of Physics and Astrophysics, University of Delhi, Delhi

(*Received July 26, 1965; Resubmitted Oct. 18, 1965*)

Concentration quenching of fluorescence in solutions gives a convenient method for the study of transfer of electronic excitation energy. The diffusion theory of concentration extinction of fluorescence worked out by Frank Wawilow and Sveshnikow taking into account the Brownian motion of the particles and collisions of the second kind, gives the following equation :

$$\frac{L_0}{L} = 1 + \frac{2p\tau_0 ckTR(\sigma_1+\sigma_2)}{3\eta\sigma_1\sigma_2} \qquad (1)$$

L_0 and L are the yields of fluorescence in the unextinguished and extinguished solutions, p the probability of extinction during one collision, K the Boltzmann Constant, T the absolute temperature, C the number of molecules in unit volume, R radius of the sphere of activity, σ_1 and σ_2 the kinetic radii of the colliding molecules and η the coefficient of viscosity. However, the experimental results on the quenching of fluorescence indicate that the above mechanism of the transfer of energy by itself is not adequate to explain the phenomenon. Forster has shown that as a consequence of the fluctuations in the distribution of the molecules of the fluorescent material in solutions which are viscous, the concentration extinction of fluorescence for individual excited molecules takes place with different probabilities. The contribution due to this towards quenching is termed 'statical extinction'. The present measurements of fluorescence yield with varying concentrations of dye stuffs in solutions having different viscosities have been undertaken to confirm the above.

The experimental set-up is the same as described earlier (Machwe *et al.*, 1964). The dyes used in the present investigation are sodium fluorescein and acraflavin. The solvent viscosity is varied by taking suitable glycerine-water mixtures. The exciting radiation is the unpolarised Hg line λ 4358Å. In Figs 1, 2, 3 and 4

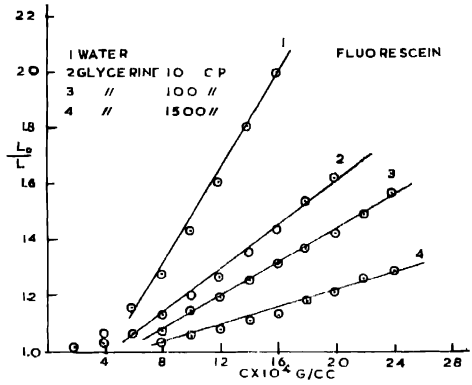

Fig. 1 *Fluorescein* Dependence of yield on concentration in (1) water, (2) water glycerine 10 cp, (3) water | glycerine 100 cp and (4) glycerine 1500 cp.

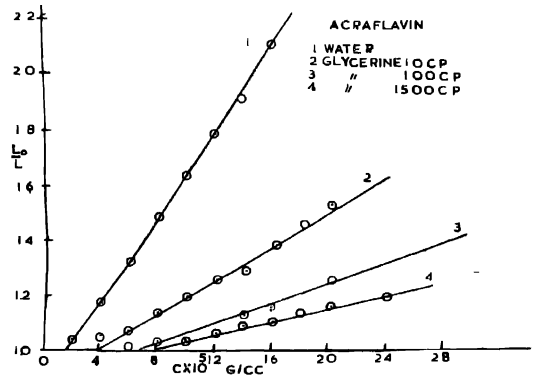

Fig. 2 *Acraflavin*. Dependence of yield on concentration in the same solvents as fig. 1.

are reproduced the date obtained by us. Figs 1 and 2 show the dependence of fluorescence yield (L_0/L) on the concentration (C) of the dissolved substance in different solvents having viscosities in the range of 1 cp to 1500 cp. Figs 3 and 4 show the dependence of yield (L_0/L) on the viscosity (η) of the solvent

It will be seen from the graph that, in the concentration region selected, a linear relationship exists between the fluorescence yield (L_0/L) and concentration (C). This agrees well with the results obtained on the basis of the diffusion theory and indicates the occurrence of collisions of the second kind. For a fixed value of η, p in Eqn. 1 remains constant and therefore, the statical extinction will have no effect on the linear relation between L_0/L and C.

The diffusion theory, Eqn 1, also predicts a linear relationship between L_0/L and $1/\eta$, but our measurements (Figs. 3 and 4) show a deviation from such a rela-

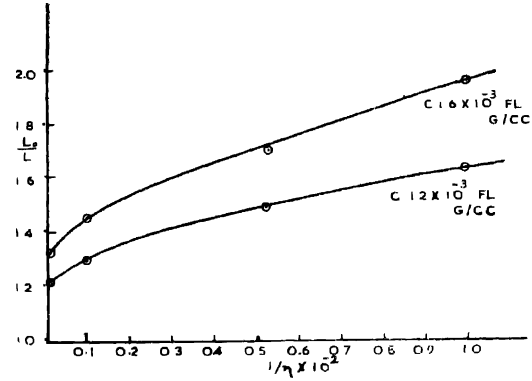

Fig. 3. *Fluorescein* : Dependence of yield on viscosity of solvent.

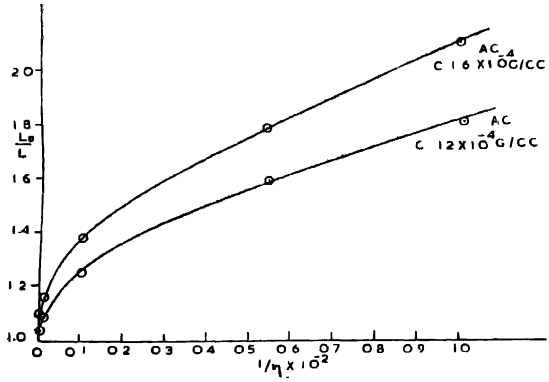

Fig. 4. *Acraflavin* : Dependence of yield on viscosity of solvent.

tionship This shows that the diffusion theory is not adequate by itself in explaining the results, when p in Eqn 1 is assumed constant. But if one considers in addition a statical extinction, the value of p will change with η and can explain the nonlinear relationship between L_0/L and $1/\eta$ Similar results were obtained by us in the case of rhodamin (Machwe *et al.*, 1964) and of anthracene by Sveshnikov *et al* (1956) So it is reasonable to assume that in the case of fluorescein and acriflavin solutions also the transfer of excitation energy takes place through the mechanism of diffusion theory as modified by considerations of fluctuations in the distribution of the solute molecules in solutions

REFERENCES

Forster, T., 1949 *Zs. Naturforsch.*, **4a**, 321.
Machwe, M K, *et al*, 1964, *Curr. Sci*, **10**, 301
Sveshnikov, B Ya, and Tishchenko, G A, 1956, *Optika Spektroskopia*, **2**, 155